GENERAL ELECTRIC

Research Laboratory

Quarterly Technical Report No. 2

PREPARATION TECHNIQUES FOR GROWTH OF SINGLE CRYSTALS OF NONMETALLIC MATERIALS

E. M. Clausen and J. W. Rutter

Contract No. AF-49(638)-1247

December 1963

Air Force Office of Scientific Research

SCHENECTADY, NEW YORK

63-GC-0260M

GENERAL ELECTRIC

Research Laboratory

REPORT NO. 63-GC-0260 M

PREPARATION TECHNIQUES FOR GROWTH OF SINGLE CRYSTALS OF NONMETALLIC MATERIALS

E. M. Clausen and J. W. Rutter

Quarterly Technical Report No. 2

Contract No. AF-49(638)-1247

Period Covered: September 1 to November 30, 1963

December 1963

Published by
Research Information Section
The Knolls
Schenectady, New York

FOREWORD

This report describes work done under Contract No. AF-49(638)-1247, ARPA Order No. 447, during the period September 1, 1963 to November 30, 1963. The work reported herein was carried out by E.M. Clausen and J.W. Rutter under the general supervision of T.A. Prater.

PREPARATION TECHNIQUES FOR GROWTH OF SINGLE CRYSTALS OF NONMETALLIC MATERIALS

E.M. Clausen and J.W. Rutter

INTRODUCTION

The work of this project is directed toward developing techniques for the growth of high-purity single crystals of nonmetallic materials. The two approaches to be used are single-crystal growth by the Verneuil technique using an r-f coupled plasma of argon as a heat source and crystal growth by the floating zone technique. The heat source for the floating zone technique will be either an oxide susceptor, such as stabilized zirconia, or direct r-f coupling to the nonmetallic material. A description of these techniques is discussed in more detail in Quarterly Technical Report No. 1.

CURRENT WORK

The work during this contract period has been divided into three general areas:

1. Improve techniques with the r-f coupled plasma torch so that single crystals are more readily attained.

2. Determine the cause and remedy for the porosity present in all crystals grown to date by this method.

3. Initiate work on single-crystal growth by the floating zone technique.

Frequently while growing a crystal by the Verneuil technique using the r-f coupled plasma as a heat source, the plasma may be extinguished when changing gas supply from one bottle to another or when large quantities of powder drop through the powder feed tube. Because of the severe heat shock, this results in ruining the crystal that has already been grown. The normal amount of argon in one gas bottle supplies enough gas to run the plasma for periods up to 5 hours. Frequently it is desirable to run the plasma for longer periods of time because slow growth rates are necessary with many nonmetallic materials. Therefore, it is necessary in many cases to change gas bottles while a crystal is growing. Because of the difference in pressure between a full bottle of gas and a near empty bottle, the plasma may be literally blown out by the high velocity of gas through the quartz tubes caused by the pressure change. A constant pressure manifold is now being used which permits changing gas supply from one bottle to another while the plasma is running. This permits the plasma to run continuously for periods exceeding 5 hours.

Large quantities of powder coming through the powder feed tube may also extinguish the plasma. This is caused by an uneven powder feed from the feed hoppers, so that rather than a steady stream of particles being fed through the

plasma the powder is fed intermittently in large quantities. An equally important result of this intermittent powder feed is that not all of the powder melts in the plasma because the normal heat flux is not large enough to cope with large transients in powder feed. Large quantities of unmelted powder hitting the top of the boule would lead to nucleation of new grains at the liquid-solid interface. To illustrate this point of unmelted powder, several boules of $CoAl_2O_4$ were crushed to a size suitable as a powder feed for the plasma. In this manner the powder used was very dense and essentially single crystal. The resultant boule was poly crystalline with many grains across the cross section. Microscopic examination of powder, which passed through the plasma but did not become a part of the boule, showed that very little of the powder melted as it passed through the torch. Most of the powder that passed through the flame looked the same as the starting powder rather than the characteristic spherical shape of melted powder. Therefore, the unmelted particles were probably nucleating new grains at the liquid-solid interface. Sintered powders in the size range of 75 to 150 microns that are free of fines are presently being used with good results. The fine particles in these powders are normally what hinder proper flow characteristics. The powder feeding has been improved with the use of a suitable vibrator such that reproducible and constant feed rates have been achieved from one run to another. With control over the powder feed rate and the withdrawal rate of the seed from the plasma flame, the growth rate of the crystal may be accurately controlled.

Porosity in the crystals grown with the r-f coupled plasma torch has been a problem since initiation of this work. There are several possible sources of this porosity such as: (1) gases that are entrapped in the sintered particles used as a powder feed may not get a chance to diffuse to the surface of the liquid cap, (2) the material that is being grown may be decomposing, or (3) the gases used for the plasma may be soluble in the melt at the very high gas temperatures attained and are precipitating out on cooling. It does not seem probable that the material is decomposing, for microscopic examination would show more than one phase present in the resultant boule. Microscopic examination of all boules grown to date shows no significant amounts of other phases present that would be characteristic of decomposition. The dense, essentially single-crystal powder of $CoAl_2O_4$ was used in an attempt to grow a single crystal with low porosity. It was felt that by using a high density powder, the porosity could be significantly reduced. This, in fact, was the result; however, as mentioned earlier, the resultant boule was highly polycrystalline because the powder was not thoroughly melted as it passed through the plasma flame. Increasing the plasma temperature to melt the powder would only result in other problems associated with crystal growth. The seed would have to be lowered away from the hotter plasma with the result being that the powder would spray more, with much of it missing the growing crystal. Therefore, other methods will have to be used to reduce the porosity.

The apparatus schematically shown in Fig. 1 utilizes the fact that a nonmetallic material may be directly r-f coupled. The apparatus is a modified Verneuil type furnace with the heat source being the sample itself. The powder is dropped from the feed hoppers through a quartz tube and onto a molten pool of the material being grown. A slight positive gas pressure is maintained in the powder feed enclosure to keep the feed tube from plugging. A quartz tube may be

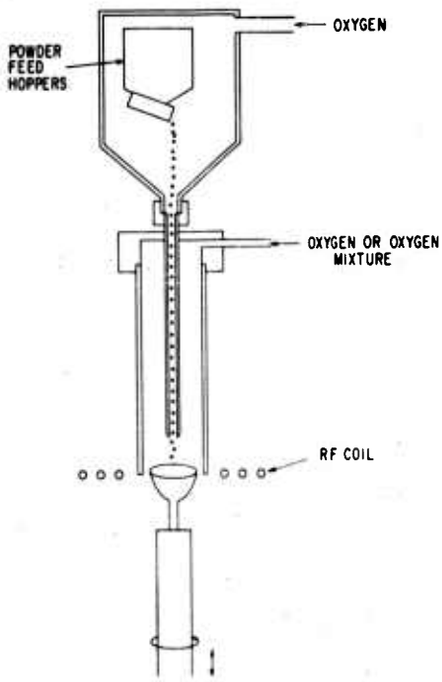


Fig. 1 Technique for single-crystal growth by the Verneuil method using direct r-f coupling.

used to enclose the crystal as it grows with a flowing atmosphere of oxygen or a mixture of gases, whichever may be desirable. One boule of nickel oxide was grown by this method and another using the plasma to determine the effect of the gases used in the plasma on the porosity of the grown boule. The samples were grown at about the same rate of 1/4 to 1/2 in/hr on seeds of polycrystalline sintered rods. Figures 2(a) and (b) show the boule as grown using the plasma torch and a cross section of the boule. Figures 2(c) and (d) show the boule as grown using direct r-f coupling and a cross section of the boule. The results show quite significantly that the specimen grown in the plasma has an extremely large amount of porosity while the specimen grown by direct r-f coupling has very little porosity. The specimen shown in Figs. 2(c) and (d) was grown in air with oxygen flowing through the powder feed tube. Another specimen was grown in roughly the same atmosphere as used in the plasma of 95% argon and 5% oxygen. The result was the same in that the boule had very little, if any, porosity. The evidence of this work points strongly to the fact that one or both of the gases used in the plasma may be soluble in the melt at the temperatures obtained. No definite conclusions can be drawn at the present; however, more work will be done in the future on this problem. If the gas solubility is the cause for the porosity, single crystals will have to be grown at much slower rates than are presently being used, to allow the gases sufficient time to diffuse out of the melt.

Toward the end of this report period, construction was completed on the equipment to be used for single-crystal growth by the floating zone technique. The equipment was checked out by moving a molten zone down a rod of nickel oxide three times. Direct coupling was achieved at 15 Mc by first coupling to a piece of metallic nickel, which fluxed the oxide to form a 1/4-inch liquid zone in a 1/4-inch polycrystalline rod. On the first two passes the zone was moved down the specimen at a speed of 1/2 to 1 in/hr. The final pass was made at a speed of 1/4 in/hr. The specimen ends were rotated both in the same direction and in opposite directions. No noticeable effect was observed on the rod as a result of changing rotation directions. After the third pass the rod was sectioned and found to contain between two and four grains across a cross section. Cleaved portions of the rod appear to have a large amount of substructure; however, this will be explored further in the following report periods. The nickel oxide rods grown to date have been done in air, but other atmospheres will be used in the future to determine the effect of the atmosphere on the growth characteristics. A single crystal will be cut from one of the rods already zone melted to be used as a seed. Once this is achieved, larger single crystals may be grown.

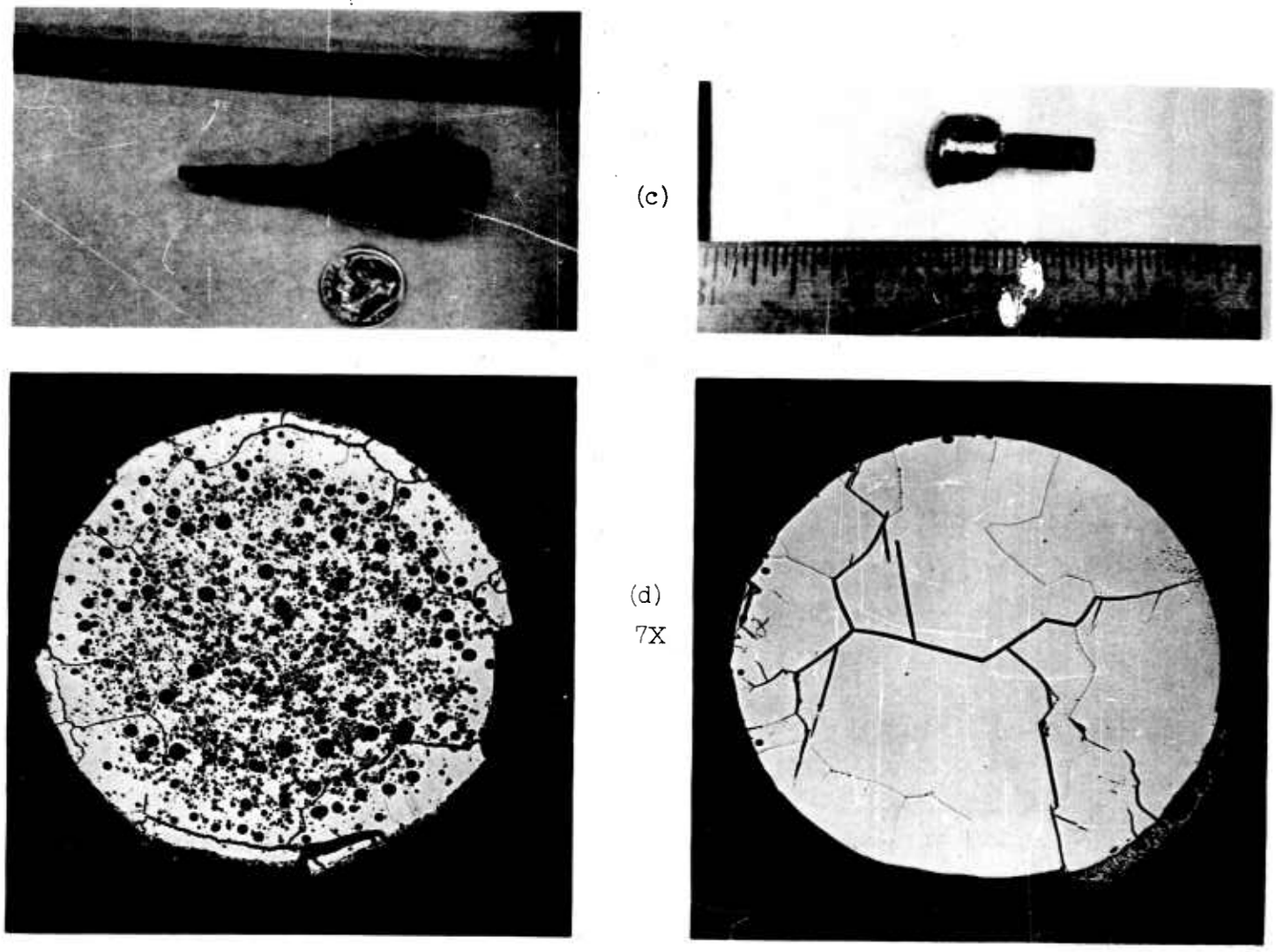


Fig. 2 Comparison of samples of NiO as-grown with the r-f coupled plasma torch and direct r-f coupling.

PROGRESS ON MATERIALS TO DATE

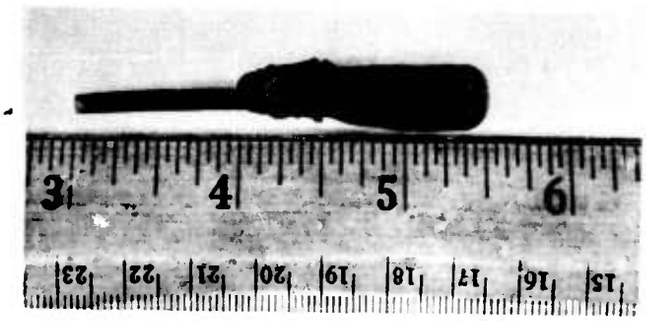
Al_2O_3

Growth of single crystals of this material was again attempted using the r-f coupled plasma torch. All crystals were grown on 1/8-inch-diameter single-crystal sapphire rods. In the beginning a relatively impure powder of 99.5% Al_2O_3 was used. Again the boiling and frothing were evident as reported in the first Quarterly Technical Report. A higher purity powder was used that was made from Linde A Al_2O_3, which is nominally 99.9% pure and has an average particle size of about 1 micron. This powder was isostatically pressed and sintered in air at 1300°C for 1 hour. The sintered mass was then crushed and sized to the suitable range for a powder feed. When this material was used as a feed, the boiling and frothing all but ceased. In effect, then, the boiling and frothing were probably caused by impurities in the residual powder. One interesting aspect to this is that an orange-colored halo seemed to surround the boule as it grew when using the more impure powder, while no halo was present when the high-purity powder was used. It was difficult to determine the exact color of the halo because dark green plastic is used as a filter for the ultraviolet light given off by the plasma, but the halo appeared orange through the dark plastic. Because sodium is invariably present in impure Al_2O_3, one may speculate that this would be sodium vapor.

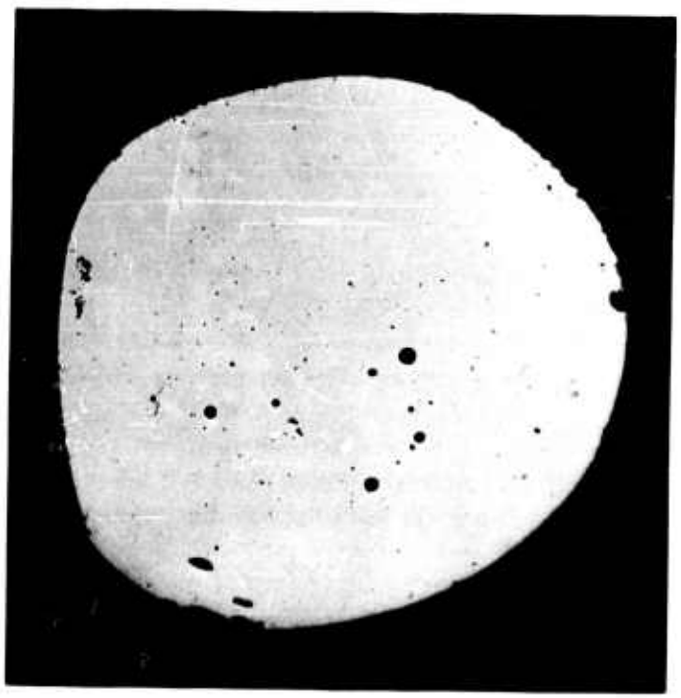
Using the high-purity powder, a single crystal of Al_2O_3 grew very uniformly although porosity was still very much in evidence. The sample also cracked owing to thermal stresses on cooling. Nitrogen was substituted for oxygen in the argon to determine if another diatomic gas would have an effect on the growth habit and reduce the porosity. No noticeable effect was encountered. The only effect noticed was that the plasma flame itself was not as hot with nitrogen as with oxygen. The seed had to be pushed up higher in the flame to keep a molten pool on top. Additional work on this material will be curtailed owing to the ready availability of these crystals by the flame fusion process. It is felt that efforts should be used to grow crystals that cannot be grown by other conventional methods.

Co Al_2O_4

Figures 3(a) and (b) are pictures of a boule of Co Al_2O_4 as grown with the plasma torch and a cross section about half way up the boule. The specimen half way up the boule is single crystal with a small amount of porosity. There were some small columnar grains growing up along the edges of the boule, which were ground off. This sample was grown at a speed of 1/2 in/hr on a polycrystalline sintered rod. Several single crystals of this material have been grown with the same result of having a small amount of porosity. As mentioned earlier, a highly dense powder resulted in a polycrystalline boule. It is presently felt that slower growth rates would result in a smaller amount of porosity. Additional work on this material has been hindered because of difficulty in fabricating a homogeneous powder. The original crystals were grown from a powder made by the coprecipitation of the hydroxides of cobalt and aluminum from sulfate solutions. This is a long, tedious method of making the material. An



(a)



(b)

12.5X

Fig. 3 Co Al_2O_4 as grown by the Verneuil method using an r-f coupled plasma as a heat source.

attempt was made to produce Co Al_2O_4 from a mixture of cobalt carbonate and aluminum oxide that was calcined at 1200°C for 4 hours. The resultant powder was not homogeneous, and crystals grown from this powder were not stoichiometric. Powders are now being fabricated by the coprecipitation method and additional work will be done on this material.

Two crystals of this material have been given to other members of the Research Laboratory staff for property measurements. Thermal conductivity measurements are presently being made on one crystal and comparisons made with other materials of this same class. Nuclear magnetic resonance studies are to be made on one crystal. The purpose of these measurements is to determine where in the lattice the cobalt and aluminum ions are located. Cobalt aluminate is thought to be a normal spinel-type structure with the Co^{+2} in the tetrahedral sites and Al^{+3} in the octahedral sites. Heat treatment and growth conditions may cause a certain amount of inversion so that cobalt may occupy some octahedral sites and aluminum occupy tetrahedral sites. The purpose of

nuclear magnetic resonance studies is to determine if there is any inversion and which is the stable phase, i.e., the inverted spinel or normal spinel.

NiO

Considerable work is yet to be done with this material by direct coupling zone melting. Figure 2 shows a comparison of two boules as grown by direct coupling and using the r-f coupled plasma torch. The sample grown with the plasma was grown on a 1/8-inch-diameter polycrystalline rod. Although Fig. 2(b) does not show the grain boundaries clearly because of the porosity, there are only seven grains in the cross section. The sample grown by direct coupling has three times as many grains, but it was grown on a 1/4-inch-diameter polycrystalline rod. The sample grown by direct coupling was controlled with a liquidus temperature of 1975° ± 20°C. Temperature measurement was made by a two-color pyrometer. The significant result of these two specimens is the difference in porosity between the two.

For growth of single crystals by the floating zone technique, a molten zone was passed down a polycrystalline rod three times. The first two passes were made at speeds of 1/2 to 1 in/hr to remove porosity and to straighten the rod. The third pass was made at the slower speed of 1/4 in/hr in an attempt to grow a single crystal. In effect, the number of grains was significantly reduced to two to four grains in a cross section. Additional work will be done on this material by seeding the rod with a single crystal cut from one of the polycrystalline rods grown to date. It is hopeful that by seeding the rod in this manner a single crystal will be the result and that growth rates of the crystals may be increased. The effect of different atmospheres on the growth characteristics will also be explored.

FUTURE PLANS

1. Work will be continued to determine the cause and remedy for the porosity that is present in crystals grown with the r-f plasma torch.

2. At the present time other materials are being fabricated into powders suitable for a powder feed. Attempts will be made to grow single crystals of these materials with the r-f plasma torch.

3. Additional work will be done to grow single crystals by the Verneuil technique using direct r-f coupling. For materials that may be directly r-f coupled, single crystals may be grown by this technique, provided suitable powders are available.

4. Work will be continued on single-crystal growth by the floating zone technique. Work will be continued on growth of nickel oxide single crystals both in different atmospheres and positive oxygen pressures.

UNCLASSIFIED